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Ruhrochemie A.G. Oberhausen-Holtan, March 29, 1939
To: Professor Martin, Dr. Hagemann, Dir. Alberts
"Catalytic Polymerization of Unsaturated Hydrocarbons"

The submitted work treats a polymerization process, by which the so-called solid phosphoric acid catalyst of Ipatieff was employed. For a better view of the total material this is divided into 3 summarized single groups, and so

- A) Polymerization of condensate naphtha
- B) Polymerization of gasol (Trans.: L.F.G.)
- C) Polymerization of condensate naphtha + gasol
 - 1) without C_2H_4 addition
 - 2) with C_2H_4 addition

Goal of the Method - Preparation of liquid, knock-resistant hydrocarbons, which lie within the boiling limits of motor fuels, starting out from a low-boiling fraction of condensate naphtha or gaseous olefins on the other hand. The inclusion of the condensate naphtha gives the possibility of transformation of these low-boiling light bodies into high boiling heavy naphtha of equal or higher octane number and with it an improvement of the specific gravity of the "F.T." (Trans.: Fischer-Tropsch?) product.

Before the subdivision in groups in the further discussion of the work, the common characteristics of the three groups of the procedure is to be anticipated here. These are:

1) The apparatus - It consists of two iron tubes each 1000 mm. long with an interior diameter of 22 mm. which are connected with one another by a strong capillary. At the beginning and end of the reaction tube is found a Hofer valve for the purpose of regulation of the addition and withdrawal of the reaction charge at constant pressure. Each tube possesses an electric heater with two measuring places for the temperature of the external jacket. On account of the small diameter, it was not possible to accomplish inner temperature measurements by means of built-in thermal elements. The heating length of the furnace amounted to ca. 1700 mm. so that the reaction space amounted to about 650 cc. The furnace was filled with a catalyst (ca. 600-700 g.).

2) Execution of the process - Out of a bomb with submerged tube the charge to be polymerized is forced into the apparatus by means of N_2 and streamed through both slightly inclined furnaces. At the end of the second furnace the released polymerized product flows through a condenser into a measuring receiver. It possesses a reflux cooler, and is closed in order to be able to measure the non-condensable products as gas.

3) Catalyst - A polymerization catalyst specified by Ipatieff was employed. It had the following composition:

60 g. magnesium chloride
50 g. magnesium oxide
100 g. kieselguhr
50 g. starch
20 g. alumina
800 g. phosphoric acid 82%

The specified amount corresponds to about one-half liter of catalyst.

4) Conditions of the experiment - Only the temperature was kept constant at 200°C for the main experiments since this proved to be the optimum for our furnaces after several test experiments. Pressure and residence duration (Trans: contact time) were greatly varied, as will be shown.

5) Method - As motor fuel only the polymers lying within the boiling limit of 200°C are important. The problem in the far-reaching working up of the olefins was as much as possible not to allow liquid polymer to go beyond the dimerization. There was introduced therein as a criterion of the strength and quality of the polymerization a ratio ($K_{\text{polymerization}}$ ratio) which shows how many volume percent of the constituents boiling over 200° correspond to the volume percent of the polymerized constituents at 70°C.

For example, a condensate naphtha boiling up to 70°C is polymerized. The boiling curve of the polymer shows at 70° 40 vol.% and at 200°C 90 vol.% distillate. In this case:

$$K = \frac{10}{80} = 1:6$$

i.e. that in a polymerization of 60 mol. % at 70°C, 10% boils over 200°C. The numerator of a good polymerization should be as small as possible, the denominator as large as possible.

A. Polymerization Condensate Naphtha

For feeling out of the whole range, a series of preliminary experiments were carried out in a standing furnace with an interior width of 50 mm. and a length of 2500 mm., which contained 1700 g. of catalyst. The pressure was varied between 1 at. - 10 atm. the temperature between 150°-250°C and the velocity of the charge between 250 cc - 800 cc. condensate/hr. It is shown that a raising of the temperature or the pressure or a lowering of the charge rate increases the polymerization. However, in the same degree the amount of the portion boiling above 200°C also increases, so that in ~~all experiments in the first furnace the average polymerization ratio was~~ 1:4, immaterial if the polymerization was high or low. So, for example, experiment 17 at 200°C, 3 atm. and 400 cc. condensate/hr. shows a $K = \frac{10.5}{45} = 1:4.2$ while experiment 19/I at 200°C, 1.5 atm. and 800 cc had a $K = \frac{5}{21.5} = 1:4.3$. The polymerization in experiment 17 was twice as large

as in experiment 19/I, while the polymerization ratio in both was practically equal.

A condensate naphtha which had the following constants was used in these preliminary tests:

Boiling initial = 25°C
 Boiling end point = 76°C
 Specific gravity = 0.6470
 Index of refraction = 1.3782
 Vapor pressure = 1.4 at 38°C
 Olefins = 84%

One obtained from it crude polynaphtha which according to the vigor of the polymerization had changed the constants, for example, as follows:

Crude Prod.	Weakly Poly.Prod.	Vigorously Poly.Prod.
Specific gravity	0.660	0.715
Refractive index	1.392	1.416
Vapor pressure	1.2	0.8
Olefins	64%	46%
Boiling point initial	25°C	32°C
Boiling point end point	25°C	320°C

The fractional distillation of this product from 20 to 20°C (Trans: obvious error in the text. Probably 20^o-70^oC) showed an almost proportional increase of the olefin refractive index and specific gravity curves.

The analysis of the true polymer product (portion boiling between 80-200°C) yielded the following data:

d ₂₀ = 0.7452	d ₂₀ = 0.7430
nd ₂₀ = 1.4255	nd ₂₀ = 1.4246
olefins = 78%	olefin = 81%
OZ = 94.5%	OZ = 94%

(Trans : OZ = octane number)

Since the polymerization ratio of the experiments in a new furnace of 20 mm. inside diameter was more favorable immediately at the start, the further experiments were carried out only in the furnace of 20 mm. i.d. described above.

For the first series of experiments condensate naphtha boiling to 80°C was introduced into the new furnace. Also here the rise of the portion boiling over 200° by vigorous polymerization can be observed, as the following Table I indicates in the lowering of the polymerization ratio.

Table I

Exp.	Conditions		Speed cc/hr.	Volume %		K - Polymerization Ratio
	Temp.	Press.		Polym.	over 200°C	
16/1	200°	1 at.	250	7	-	0:7
16/2	"	2 at.	"	13.5	1.5	1:9
16/3	"	4 at.	"	17	2	1:8.5
16/4	"	10 at.	"	31	8	1:4.0

For all that, the polymerization in all experiments was small; the polymerization ratio, on the other hand, significantly better than in the first furnace.

For the second series of experiments a 20-70° boiling fraction of a previous polymerization (5 at. 200°C, 400 cc. K = 1.5) was utilized as the charge. Thereupon an interesting observation was made. While in the other polymerizations up to 10 atm. the polymerization ratio remained almost constant here it becomes ever better on utilization of higher pressures. As the supplement I shows the boiling curves intersect between 100-180° in order to rise steeper and more rapidly at higher pressure. The following Table II renders the rise of the polymerization ratio well.

Table II

Exp.	Conditions		Speed cc/hr.	Volume %		K - Polymerization ratio
	Temp.	Press.		Polym.	over 200°C	
20/1	200°	4 at.	250	22	3	1:7.3
20/2	"	10 at.	"	42	6	1:7.0
20/3	"	20 at.	"	43.5	4.5	1:9.7
20/4	"	50 at.	"	48	4	1:12
20/5	"	100 at.	"	41	2.5	1:16.4

One sees here in spite of a vigorous polymerization an improvement of the polymerization ratio which is striking at high pressure as experiment 20/5 shows. This has its basis thereon that on use of 100 at. pressure, the polymerization of light naphtha at 200°C no longer exists in the gaseous but completely in the liquid phase. The application of still higher pressure - we have gone up to 150 atm. - showed itself as aimless, as was to be foreseen.

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Continuation of "Polymerization of Unsaturated Hydrocarbons"

The application of high pressure was also used now in the polymerization of condensate naphtha. It was to establish a much greater polymerization and indeed at increasing pressure of 10 atm. to 100 atm. 31 volume % polymer to 58 vol.% whereupon the polymerization ratio increased from 1:4 to 1:6.5. In spite of doubled polymerization, the volume % of components boiling above 200°C rose only from 8% up to 8.5 volume %. The red curve in supplement II again yields a good polymerization ratio. One sees from it that at establishing greater polymerization (at 10 atm.) it rises steeply, in order to remain afterwards almost equal in spite of increase of the polymerization.

A further advantage of the high pressure was the greater amount of charge and connected with it the greater amount of condensate per hour which one can obtain at equal contact time. With a greater charge rate goes hand in hand a further employment of the polymerization ratio. Therewith, the characteristics for the further course of the work were given:

1. higher pressure
2. greater amount of charge

Since good results were realized in the second series of experiments with a fraction of the pre-polymer, a condensate naphtha treated in the cold with "Tonsil" (Trans: a certain acid-treated clay) was introduced. We believed, namely, that by the pre-polymerization the gum and resin-forming materials would be dissolved out and wished to reach this same effect by the treatment with "Tonsil" in the cold. This was not realized. The polymerization ratio was not improved and the boiling end point even pushed out yet to 270°. (Table III, graphically: supplement II). Also an olefin-poor mixed charge-obtained from 3 parts condensate naphtha and one part pre-polymer fraction of 20°-70°- showed no change in the polymerization ratio. (Table III, graphically: supplement II).

From the attached Table III, is to be seen that also by application of high pressures a change of the temperature or the speed of the charge causes a shift of the polymerization, without markedly changing the polymerization ratio. This becomes only more favorable by introduction of pre-polymerized products. After proof of influence of temperature, pressure and speed in the one-step polymerization we came by means of this knowledge to the two-step.

At first we carried out the two-step polymerization so that we introduced the condensate naphtha weakly polymerized and the fraction 20-70° of the pre-polymer (ca. 90%) into the same reaction furnace as in the main polymerization under mild conditions (150°, 1 atm. 100cc) for the

main polymerization. It is shown, thereby, that a two-step polymerization and indeed weak pre-polymerization with strong main polymerization showed better results only at greater charge rate (2000 cc/hr), while the simple polymerization at a speed of 1000 cc/hr cuts off somewhat better. The supplement V graphically presents the ratio of the two-step polymerization in comparison with the one-step polymerization.

A second method which can be claimed as a pre-polymerization was the treatment of the condensate naphtha with "Granusil" in the vapor phase. For this and the light naphtha was allowed to flow through a superheater into the reaction tube proper which was filled with "Granusil". The throughput occurred at a temperature of 225° and a speed of ca. 2000 cc/hr.

Since thereby naphtha was obtained, which had the boiling end point of 198-220°, no loss resulted in relation to motor fuel. In the starting of the furnace one obtains a small weight difference between the entering charge and the end product which continually became smaller (decreasing C-separation) and completely discontinued after several liters of naphtha throughput, so that also in this relationship, no noteworthy losses occurred since no gas cleavage occurred. The constants of the products before and after the treatment were:

Initial boiling	38°	Initial boiling	38°
End boiling	73°	End boiling	198°
Gas loss	8.5%	Gas loss	5.5%
d ₂₀	0.6602	d ₂₀	0.6723
nd ₂₀	1.3871	nd ₂₀	1.3911
olefins	80%	olefins	77%

The product treated previously was distilled to 70° (it shows a boiling curve up to ca. 200° whereby ca. 85% went over up to 70°) and the distillate introduced to the main polymerization. There was then obtained an average polymerization ratio of 1:10.5 (graphic supplement III.) As supplement V shows the ratio at best to lay in this combination, "Granusil" treatment as weak pre-polymerization with following strong phosphoric acid polymerization.

On the other hand, if the pre-polymer (boiling end point 204°) after the "Granusil" treatment is not distilled to 70°, but directly introduced into the main polymerization, so falls the polymerization ratio--also by application of different charge rates--again to average 1:6 (graphic representation: supplement IV).

Even an increase of the speed to 4500 cc/hr, the maximum which our apparatus could reach, yielded in weak polymerization the formation of products which boiled over 200°C. It must, therefore, be accepted that in the naphtha charge are materials which come together to higher polymers with much greater speed than the normal polymerization occurs. Therefore, it is not possible also in strong polymerization to keep the boiling end point accurately at 200°C. In the experiments with the two-step process with Granusil we obtained products with boiling end points which lay between 210-220°, accordingly can be utilized practically as a motor fuel.

B. Polymerization of Gasol (L.P.G.)

For carrying out this experiment, the same reaction furnaces, as previously mentioned, were taken, and the influence of temperature, pressure and speed of charge were systematically investigated. The numerical compilation of the characterized experiments are shown in Table IV. The essential observations, which are yielded from it, should be singly counted.

The Gasol charge contained 60% $C_3H_6 + C_4H_8$ and 4.5% C_2H_4 .

Change of Speed at 100 at. and 10 at.

In the first series of experiments of the table, the rate of the charge/hr. was varied at equal temperature (200°C) and equal pressure (100 at.). One recognizes very distinctly the proportionate decrease of the $C_3 + C_4$ polymerization with increasing amount of condensate/hr. while in the C_2H_4 polymerization between 500 and 1000 cc polymer/hour large irregular decrease takes place.

At low pressure (10 at.) the rate change is connected with a great decrease in the total polymerization. The rate of 600 cc condensate/hr. utilized in experiment 47/III was the largest which could be reached at this pressure.

Change of the Pressure at 250 cc and 1000 cc Condensate/hr.

An increase of the pressure at lower rate is followed by a uniformly rising polymerization of the $C_3 + C_4$ olefins, while the irregular increase of the polymerization of C_2H_4 here lies between 10 and 50 atm.

One sees from the compilation certain parallels between the two groups: change of rate and change of pressure. As example follow the data of 2 polymer-naphthas (crude product) obtained from gas oil:

weakly polymerized (48/II)		strongly polymerized (44/I)	
sp. gravity	= 0.7155		0.7433
refractive index	= 1.4164		1.4273
olefins	= 79%		70%
boiling point			
Initial	= 23°		35°
boiling point			
End	= 252°		261°
gas loss	= 7%		6%
50% point	= 107°		137°
until 200°C	= 91 vol. %		87%

The octane number of all polymeric naphthas from gasol lies between 96-98 according to the research method.

C. Polymerization of Condensate Naphtha and Gasol

1) Without addition of C₂H₄

A mixture proportion of 1:1 was prepared in the bomb. The gasol analysis yielded: C₃H₆ + C₄H₈ = 43%. As brought forth from Table V, one finds again exactly the same products as in the polymerization of gasol alone. So, for example, the equal decrease of the C₃+C₄ polymerization by the increase of the charged amount at 100 atm., of the rapid decrease by the change of rate at low pressure etc. Also no essential displacement of 200° point is to be noted by introduction of this mixture. It lies, for example, in a strong polymerization (92% olefin working up) at 86 vol.% while at a weaker polymerization (23% working up of the olefin) it rises to 93 vol.%. One also sees here the most favorable results by application of high pressure combined with greater amount of charge.

2) With addition of C₂H₄

Since in the mixture of gasol and condensate naphtha, the C₂H₄-content was so low, that one could not exactly measure the course of the C₂H₄ polymerization, a three-way mixture was prepared for clarification of this question which appeared important for the direct treatment of cracked gases in the "Poly-plant" during conservation of the ethylene on the one hand and for the clarification of the question of the possibility of the complete co-polymerization of the ethylene on the other hand. The gas mixture had the following olefin composition: C₃H₆ + C₄H₈ = 42.1% and C₂H₄ = 22.2%.

Table VI shows the series of experiments with increasing pressure and increased amount of charge. The polymerization of the C₃+C₄ olefins proceeds in the known ways while the polymerization of C₂H₄ is significantly less, but also grows with increasing C₃ polymerization. At low pressures 5-10 atm., it is practically zero in order to reach to 18% at a 90% C₃+C₄ polymerization.

Table VII shows the result of the investigation of three poly-naphthas from gasol and gasol plus condensate naphtha in different proportions.

From Table IX is to be learned the knock resistance of different naphthas.

Table X shows several residual gas analyses of the polymerization of condensate naphtha and gasol, and gasol alone.

Table VIII renders the properties of several naphthas cut to 200°C and the higher poly-products.

Experiences with the phosphoric acid catalyst

Essentially for its effectiveness and long stability is the form in which the phosphoric acid exists. The correct choice of dehydration is decisive therefor. We have found on optimum at 250°. In one experiment the temperature was allowed to rise to 310°. The effectiveness of the catalyst decreased rapidly.

Several experiments by additions of small amounts of water (0.5-1% of the throughput) in order to retain activity for a longer time were wrecked after a short time by the limited diameter of 20 mm. of our oven by obstruction of the passage with stuck-together catalyst. For this purpose it was necessary to lead in direct steam or send the water through a superheater. These experiments, which lead to very good results, will be treated in the following work regarding polymerization.

Since we did not allow the reaction furnace to run continuously, it was flushed with nitrogen at somewhat elevated temperature, about 230°C each day at the end of the experiment in order to free it entirely of charge. It is possible that this process at the same time represents a kind of regeneration of the catalyst, because we already have the last catalyst in use the fourth week with an operating hour number of 142, without its effectiveness diminishing.

Summary:

The polymerization of olefins with solid phosphoric acid catalyst is a process patented by U.O.P. The application of high pressure shows better results, according to our investigations, since polymerization in the liquid phase strongly represses over-polymerization. A further advantage is the increase of the amount of charge. Recently this process of high pressure polymerization which was independently found by us, was applied on a large scale by U.O.P.

Explanation for the several supplements

Supplement I, III and IV render the boiling curves of the polymer products obtained from condensate naphtha and the polymerization ratio obtained at 70°C.

Supplement VI shows the boiling position of the poly-products from the mixture of condensate naphtha and gasol in the proportion of 1:1 with the corresponding polymerization ratio and the value of the C₃-C₄ polymerization.

Supplement VII illustrates the boiling curves of the gasol poly-product with gas analysis and C₃-C₄ working up in vol.%.

Supplement II presents the polymerization ratio (vol.% over 200°C; vol.% polymerization at 70°C) as a function of pressure, temperature and amount of charge by differently-treated condensate naphthas. Here it is very clear (on the red line) to recognize the advantage of the application of high pressure to polymerization. While at point P₁ (200°, 10 at. 250 cc) the 8 vol.% of constituents boiling over 200° coming out at 31% vol.% polymerization rises in point P₂ (200°C, 100 at. 250 cc) in spite of a polymerization increase to 55%, to only 8.5 vol.% of the portion boiling over 200°C. i.e. at a total increase of the polymerization of ca. 44%, it comes to only a 6% (6% of 8%) increase of the constituents boiling over 200°.

Supplement V shows the polymerization ratio in relation to pressure charge and temperature of several condensate naphthas in one step and two step polymerization process. One sees that the two step polymerization cuts off best (red line) with a "Granusil" pre-polymerization. In a 47% polymerization the constituents boiling over 200° amount to only 4.5% in this case and increase to 8 vol.% in a 63% polymerization (i.e. a complete working up, since there were no more olefins in the condensate naphtha).

Information Content of the Tables

Table

- III - Single step condensation of condensate-naphtha
- IV - Gasol polymerization
- V - Polymerization of condensate naphtha and gasol without C₂H₄
- VI - Polymerization of condensate naphtha and gasol with C₂H₄
- VII - Properties of several poly-naphthas boiling to 200°
- IX - Octane number data of several poly-naphthas
- X - Residual gas analyses.

Table III

Completion of several experiments of the single step polymerization carried out at different temperatures, pressure and charge.

Exp.	Charge	Conditions			Vol. %		Ratio K
		Temp. C	Pressure(at)	Cond.cc/hr	Polym.	over 200°	
23/III	Condensate naphtha	150	100	1000	39	6.5	1:6
23/III	"	150	100	250	51	8.5	1:6
23/II	"	200	100	1000	52.5	8.5	1:6.2
23/I	"	200	100	250	55	8.5	1:6.5
28/II	"	200	130	3000	55	8.5	1:6.5
28/III	"	250	130	3000	65	10	1:6.5
28/IX	"	250	130	4500	59.5	9	1:6.6
26/I	Condensate Naphtha treated with Tonsil	200	100	250	62	10	1:6.2
26/II		200	100	1000	55.5	8.5	1:6.5
26/III		250	100	1000	84	14	1:6.0
25/I	Condensate naphtha 3 parts and fract. 20-70° Of a pre-polymer	200	100	250	50.5	9	1:5.6
25/II		200	100	1000	40.5	7	1:5.8
25/III		150	100	1000	30.5	5	1:6.1

Table IV

Compilation of several experiments of gasol polymerisation.

Gasol: 60% $C_3H_6 + C_4H_8$, 4.5% C_2H_4

Exp.	Conditions			Polymerisation of $C_3H_6 + C_4H_8$	Polymerisation of C_2H_4	Remarks
	Temp.	Pressure	cc/hr			
44/I	200	100	250	90%	61%	
44/II	200	100	500	81%	48%	
44/III	200	100	1000	70%	16%	Change of rate at 100 atm.
48/I	200	100	1000	70%	16%	
48/III	200	100	1500	63%	missing	
48/II	200	100	2000	56%	14%	
47/I	200	5	250	73%	12%	Change of pressure at 250 cc
47/II	200	10	250	80%	13%	
47/III	200	10	600	39%	0%	
47/IV	200	50	250	92%	66%	
47/V	200	50	1000	46%	0%	Change of pressure at 1000 cc
47/VI	200	100	1000	71%	17%	
47/II	200	10	250	80%	13%	Change of rate at 10 atm.
47/III	200	10	600	39%	0%	

Tables V and VI

Polymerisation of Condensate Naphtha and gasol

1) Without addition of C_2H_4 Gasol = $C_3H_6 + C_4H_8 = 43%$ $C_2H_4 = 0.5%$

Exp.	Conditions			Polymerization of $C_3H_6 + C_4H_8$	Polymerization of C_2H_4	Remarks
	Temp.	Pressure	cc/hr			
49/V	200	100	250	92.5%	Because of the small amount of 0.5%, exact measurements not possible.	
49/VIII	200	100	500	82%		
49/VI	200	100	1000	65%		
49/VII	200	100	2000	23%		
49/II	200	10	1000	5.8%		

2) With addition of C_2H_4 Gasol: $C_3H_6 + C_4H_8 = 42.1%$ $C_2H_4 = 22.2%$

52/I	200	5	150	50%	0%
52/II	200	10	250	55%	1%
52/III	200	50	250	89%	11%
52/IV	200	50	500	72%	11.5%
52/V	200	50	1000	51%	5.3%
52/VI	200	100	250	90.5%	18.0%
52/VII	200	100	500	80%	14%

Table VII

Investigation of 3 poly-naphthas:

G = poly naphtha from gasol, refined over "Granusil", distilled to 165° C.

G₁ = poly naphtha from gasol and condensate-naphtha (1:1) mixture of fraction 20-70° and 70-200° C in the ratio of 1:1, refined over Granusil, distilled to 165° C

G₂ = poly naphtha as G₁ only the mixture ratio of the fractions 1:2

Designation	G	G ₁	G ₂	Engler Analysis			
				Vol. %	G	G ₁	G ₂
D ₂₀	0.6871	0.6967	0.7010	5	48	52	56
ND ₂₀	1.4106	1.4052	1.4082	10	52	56	62
Raid pressure	0.68/38°	0.47	0.49	20	58	65	91
Olefins (Kattw.)	77%	67%	57%	30	67	72	78
Iodine Number	253.5	227.2	229.0	40	74	79	87
*Octane Number	Test motor in repair			50	81	89	98
*Resin-test	205.5mg/100cc	15.5	25.5	60	89	102	109
Boiling-initial	36°	38°	40°	70	99	121	126
Boiling end	157°	178°	176°	80	112	137	137
Gas loss	3%	3%	3%	90	127	152	152
50% Point	81° C	89°	98°	95	146	157	156
95% Point	132° C	160	157°				

* Octane Number: motor method

* Resin test: Bomb test method, original + 0.02g cresol/100 cc
Ind. Time min. G = 180, G₁ = 250, G₂ = 240

Table VIII

Properties of several naphthas - out to 200° C

Conditions of Experiment	5 at. 200° C 400 cc/hr.	5 at. 195° C 250 cc/hr.	100 at., 200° C 250 cc/hr.	100 at., 200° C 500 cc/hr.
Charge	Condensate naphtha	Condensate naphtha and gas oil	Condensate naphtha	Gasol
d ₂₀	0.6886	0.6997	0.7278	0.729
nd ₂₀	1.4006	1.4048	1.4230	1.4190
Raid pressure 30° C	0.95	0.88	---	---
Olefins %	72%	66%	57%	72%
Octane number	94	89	90	96.5

The higher poly-fractions of an initial boiling of 220°C and boiling end point of 270° give the following constants:

$$d_{20} = 0.84 - 0.85$$

$$n_{D20} = 1.47 - 1.48$$

$$\text{olefins} = 86-88\%$$

Table IX

Compilation of several experiments with data on the octane number (research):

Exp.	Charge	Conditions			Fraction	Octane Number
		Temp.	Pressure	cc/hr		
4	Condensate-Naphtha	200°	5 atm.	400	to 200°	89.5
15	"	200	5 atm.	400	curde prod.	93.5
15	"	200	5 atm.	400	70-200°	94
23/I	"	200	100 atm.	250	70-200°	94.5
38/III	"	200	100 atm.	1000	to 200°	91.5
35/I	2 step polymer Condensate naphtha	200	100 atm.	1000	to 200°	89.5
9	Condensate naphtha and gasol	200	5 atm.	250	to 200°	89
44/II	gasol	200	100 atm.	250	to 200°	96.5
44/III	gasol	200	100 atm.	500	to 200°	96

Table X

Residue gas analyses

- A) Polymerization of condensate naphtha: ng gas evolution
 B) Polymerization of gasol: Exp. 44/I (200, 100 atm., 250 cc/hr)

Gas Charge:		Exhaust Gas	
CO ₂	0.2%	CO ₂	0.4
C ₃ H ₆ + C ₄ H ₆	60.0%	C ₃ H ₆ + C ₄ H ₆	13.3
C ₂ H ₄	4.0%	C ₂ H ₄	3.4
C _n H _{2n+2}	35.0%	C _n H _{2n+2}	81.2
CO	0.0%	CO	0.1
H ₂	0.0%	H ₂	0.0
N ₂	0.8%	N ₂	1.7

L.G. = 2.1

L.G. = 2.2

(Trans; L.G. = Sp.gr. referred to air?)

C) Polymerisation of Condensate naphtha and gasol; Exp.: 49

Gas Charge		Exhaust gas: 49/I (250 cc/hr.)		(100° C, 100 atm.) 49/V' 250 cc/hr.)	
CO ₂	= 2.7%	CO ₂	= 3.3%		3.9%
C ₃ H ₆	= 43.0%	C ₃ H ₆	= 20.0% (67% polymerization)		5.4% (93% poly.)
C ₂ H ₄	= 0.5%	C ₂ H ₄	= 0.7% (no polymerization)		0.6% (15% poly.)
L.G. = 2.0		L.G. = 2.04		L.G. = 1.99	

D) Polymerisation of gasol and ethylene; Exp. 54

Gas Charge		Exhaust gas I. (200 cc/hr.)		200°, 50 atm. IV 250 cc/hr.	
CO ₂	= 0.0%	CO ₂	= 0.0%		0.0%
C ₃ H ₆	= 29%	C ₃ H ₆	= 14.0% (60% C ₃ -poly.)		17.7% (47% poly.)
C ₂ H ₄	= 34.4%	C ₂ H ₄	= 34.5 (17% C ₂ -poly.)		38.6% (4% poly.)
<p style="text-align: right;">200°, 5 atm. II 250 cc/hr. 0.0% 14.1% (60% C₃ poly.) 36.5% (11% poly.)</p>					

Frames 44 - 50 are graphs

Translated by Dr. H. Cohen - 1/22 and 2/1/47

Checked by G.M. - 2/4-5/47

Requested by R.F. Marschner

"Katalytische Polymerisation von ungesättigten Kohlenwasserstoffen".

(I. Teil)

Bayerchemie Aktiengesellschaft.

Oberhausen-Holten

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20 pages, 7 graphs